(CONVENTION. By one or more persons and/or a Company.) Form 4

COMMONWEALTH OF AUSTRALIA

567787

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

26.12.84.

LODGED AT SUB-OFFICE
28 DEC 1984
THE COMMISSIONER OF PATENTS

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address (es).

We (1) ATOCHEM,
of 12-16 Allee des Vosges, 92400 Courbevoie, France

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)
PROCESS AND PRODUCT FOR BLEACHING OF CHEMICAL PAPER-MAKING PULPS

(3) Here insert number(s) of basic application(s)

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered (3)
83 20990

(4) Here insert Name of basic Country or Countries, and basic date or dates

for a patent or similar protection made in (4) France
on 29th December 1983

Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys, 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 24th day of December 1984.

(5) Signature (s) of Applicant (s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association

(5)
ATOCHEM
by James Murray
James Murray

To:
THE COMMISSIONER OF PATENTS.

(CONVENTION. Company.)

Form 8

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1960

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

(1) Here insert (in full) Name of Company

In support of the Convention Application made by (1) ATOCHEM

(hereinafter referred to as the applicant) for a Patent

(2) Here insert title of Invention.

for an invention entitled: (2) PROCESS AND PRODUCT FOR BLEACHING OF CHEMICAL PAPER-MAKING PULPS

(3) Here insert full Name and Address of Company official authorized to make declaration

I, (3) JEAN LEBOULENGER,

of 12-16 Allee des Vosges, 92400 Courbevoie, France

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.

(4) Here insert basic Country or Countries followed by date or dates and basic Applicant or Applicants.

2. The basic application as defined by Section 141 of the Act was made in (4) France on the 29th day of December 1983 by ATOCHEM

~~on the~~ ~~day of~~ ~~19~~ ~~by~~

(5) Here insert (in full) Name and Address of Actual Inventor or Inventors.

3. (5) BERNARD DUBREUX, "Le Grillon", Tour E, Chemin de Chantegrillet, 69340 Francheville Le Bas, France and JEAN-PIERRE SCHIRMANN, 4º Chemin de la Glaciere, 69600 Oullins, France

~~is~~/are the actual inventos of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of the said actual inventors

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Courbevoie, France this 20th day of November 1984.

(6) Signature.

(6) Jean LEBOULENGER

To: THE COMMISSIONER OF PATENTS.

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(54) Title
PROCESS AND PRODUCT FOR BLEACHING OF CHEMICAL PAPER-MAKING PULPS

chemical pulp

(56) Prior Art Documents
US 437813
US 3472813

(57) Claim

1, A process for obtaining a high delignified bleached chemical pulp having a kappa index below 10 in a single stage directly from an unbleached chemical pulp while at the same time returning directly recyclable effluents into the bleaching operation comprising contacting said pulp with an aqueous bleaching solution at a temperature from 70°C to 100°C for a time sufficient to bleach said pulp to the degree desired, said aqueous bleaching solution having a pH of from 11 to 11.5 comprising, for each 100 parts by weight, hydrogen peroxide in an amount effective to bleach the pulp, at least one alkaline agent in amount sufficient to maintain the pH between from 11 to 11.5, at least one alkali metal silicate in an amount expressed in SiO_2 at least equal to 0.3% by weight, at least one magnesium salt and at least one calcium salt, in a quantity such that the concentration by weight of each of said alkaline earth metals is between 0.05% and 1%, and at least one sequestering agent capable of maintaining said alkaline earth metal ions in the dissolved state in an overall concentration of sequestering agent of at the most equal to 10% by weight.

COMMONWEALTH OF AUSTRALIA 567787 Form 10

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

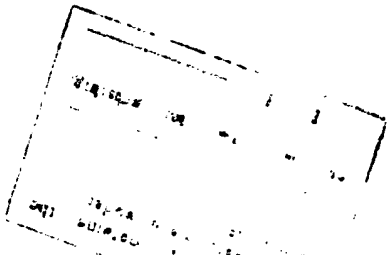
Application Number:
Lodged:

Class Int. Class

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :



37243/84

Name of Applicant : ATOCHEM

Address of Applicant : 12-16 Allee des Vosges, 92400 Courbevoie France

Actual Inventor: BERNARD DUBREUX and JEAN-PIERRE SCHIRMANN

Address for Service : **EDWD. WATERS & SONS,**
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

PROCESS AND PRODUCT FOR BLEACHING OF CHEMICAL PAPER-MAKING PULPS

The following statement is a full description of this invention, including the best method of performing it known to :-

BACKGROUND OF THE INVENTION

The present invention concerns a process and product for the bleaching of chemical paper and paperboard pulps by hydrogen peroxides; hereinafter referred to as chemical paper-making pulps.

The bleaching of such chemical pulps; that is to say, unbleached cellulose pulps obtained by the cooking of lignocellulosic materials according to the so-called sulfite process, sulfate process or Kraft process, sodium hydroxide process or carbonate process is generally practised in industry with the use of chlorine or chlorinated derivatives like chlorine having an oxidizing character; such as chlorine dioxide, ClO_2, or sodium hypochlorite, NaOCl.

None of these oxidizing agents, however, is capable of ensuring a satisfactory bleaching result alone, in a single operation. It is necessary to operate in several distinct stages and with intermediate operations such as; in particular, so-called alkaline bath extraction operations. The effluents resulting from such operating sequences are very highly colored, polluting, and corrosive. They can even involve explosion risks during the course of the reagent regeneration cycle. In particular, they contain large quantities of chlorinated organic products and of chloride ions. Because of this, they can neither be discarded nor recycled without resorting to complex and costly treatments.

The use of non-chlorinated oxidizing agents, especially oxygen or hydrogen peroxide has been envisioned in order to avoid the drawbacks cited above. The use of oxygen compels operation under pressure and is difficult and because of this, has known only a limited development.

Hydrogen peroxide can be used at atmospheric pressure in conventional bleaching equipment. Its direct use on unbleached pulps having a kappa index of the order of 30, however, has not permitted obtaining treated pulps of a kappa index below about 20-25. A supplementary stage

of pretreatment of the pulps in acid medium, as described in Japanese Patent Nos. 76/102,103 and French Patent No. 77,24131 permits improving the result but, in the same manner as all of the known bleaching processes resting on alternating stages in acid bath and in alkaline bath, does not permit avoiding the problems raised by the discarding of the recycling of the liquors after use, nor attaining low kappa degrees for the pulps treated.

SUMMARY OF THE INVENTION

The process and product according to the present invention make it possible to ensure obtaining bleached cellulosic paper-making pulps having a kappa index below 10, while at the same time delivering directly recyclable effluents into the bleaching operation.

A process for obtaining a high delignified bleached chemical pulp having a kappa index below 10 in a single stage directly from an unbleached chemical pulp while at the same time returning directly recyclable effluents into the bleaching operation comprising contacting said pulp with an aqueous bleaching solution at a temperature from 70°C to 100°C for a time sufficient to bleach said pulp to the degree desired, said aqueous bleaching solution having a pH of from 11 to 11.5 comprising, for each 100 parts by weight, hydrogen peroxide in an amount effective to bleach the pulp, at least one alkaline agent in amount sufficient to maintain the pH between from 11 to 11.5, at least one alkali metal silicate in an amount expressed in SiO_2 at least equal to 0.3% by weight, at least one magnesium salt and at least one calcium salt, in a quantity such that the concentration by weight of each of said alkaline earth metals is between 0.05% and 1%, and at least one sequestering agent capable of maintaining said alkaline earth metal ions in the dissolved state in an overall concentration of sequestering agent of at the most equal to 10% by weight.

The product of this invention comprises the above-set forth novel bleaching solution.

DETAILED DESCRIPTION

With respect to the bleaching solution it must contain the hydrogen peroxide, alkaline agent, alkali metal silicate, a magnesium and a calcium salt, and a

sequestering agent for the alkaline earth ions.

The hydrogen peroxide concentration in the bleaching bath is the one commonly adopted in this industrial area. In general, it does not exceed 1% by weight and most often is ~~between~~ from 0.02 ~~and~~ to 0.5% by weight for each 100 parts by weight of the bath.

The concentration by weight of the alkali metal silicate, expressed as SiO_2, is at least 0.3% to, for reasons for economy, below 20% by weight and most often is below 5%. Most suitably, sodium silicate is used.

The most suitable calcium salts and magnesium salts are those whose anion presents the best inertness to hydrogen peroxide under the conditions of execution of the process of the invention; such as, for example, the chlorides.

The sequestering agent or agents of the magnesium and calcium ions are, for instance, selected from among the alkali metal polyphosphates and pyrophosphates, nitrogen-containing acids such as ethylenedaminetetra-acetic acid, diethylenetriaminepentaacetic acid and nitrilotriacetic acid, or their salts, monomeric or polymeric phosphoric acids, polyelectrolytes such as poly-a hydroxyacrylic acid and the corresponding lactone.

While any conventional alkaline agent can be used to attain and/or maintain the alkaline pH, sodium hydroxide and sodium carbonate are preferred because of their low cost.

When the process according to the invention is carried out at a temperature below 70° C., the bleaching obtained is excellent, but to obtain such bleaching effect requires a long treatment time rapidly making the process economically prohibitive. When the process of the invention is carried out at a temperature above 100° C., the decomposition of the hydrogen peroxide rapidly becomes troublesome. The preferred temperature zone is from 85° C. to 95°C.

Although the method of forming the bleaching bath is not critical, it is preferred to proceed with the solubilization in an aqueous medium of the calcium and magnesium salts in the presence of an agent or agents sequestering these alkaline earth metal ions, to then introduce into the solution thus obtained the alkaline metal silicate in the form of a concentrated aqueous solution, and then the hydrogen peroxide solut[illegible]or to bringing the pH of the mixture to a value from 11 [illegible]5 with the help of the alkaline agent such as sodium hydroxide or sodium carbonate.

The contact of the cellulosic pulp to be bleached with the bath constituted for this purpose, whose duration may vary in particular as a function of the temperature, but generally does not exceed about ten hours, is carried out either in batch manner or in continuous manner, by the passage of the bleaching solution through a solid phase constituted of the cellulosic material; i.e., by the intimate mixing of this solution with this solid phase.

In the first case, that is to say, in a percolation technique, the weight ratio of bleaching solution/solid material can be from 10 to 100 and preferably from 15 to 50. In the second case, this ratio can be from 4 to 100 and preferably from 8 to 20.

The invention will be further described in connection with the following examples which are set forth for purposes of illustration only.

EXAMPLE 1

20 g of unbleached cellulosic pulp coming from a Kraft boiling process of resinous material and having a kappa index equal to 30 are treated by percolation, at 90°C, for 8 hours, with the help of 500 g of an aqueous bleaching solution of a pH kept constant at a value from 11 to 11.5 by the addition of sodium hydroxide, circulating in a closed loop at a rate of 500 ml/h of hydrogen peroxide concentration kept constant by the

addition of this reagent, and containing, by weight:

Sodium silicate (expressed as Na_2O, 3.36 SiO_2)	=	1.7%
Calcium (in the form of $CaCl_2$)	=	0.3%
Magnesium (in the form of $MgCl_2$)	=	0.15%
Sodium tripolyphosphate	=	0.6%
Sodium hydroxide	=	0.4%
100% hydrogen peroxide	=	0.34%

After treatment, the pulp has a kappa index of about 8, the quantity of hydrogen peroxide consumed in order to reach this result representing only 4% by weight of the pulp used.

EXAMPLE 2

By operating as in Example 1 and by using as the bleaching solution the solution having served to treat the load of unbleached pulp of Example 1, a second load of unbleached pulp is treated and then a third one. At the end of this third operation it is observed that the bleaching bath has preserved its entire effectiveness since the treated pulp has a kappa index of 8 while the consumption of hydrogen peroxide is 4.1% by weight with respect to the weight of the pulp used.

EXAMPLE 3

10 g of unbleached cellulosic pulp of the same origin and the same kappa index as in Example 1 are mixed with 100 g of solution of the same composition by weight as in Example 1. The mixture is kept at 90°C. for 10 hours with introduction, after 5 hours, of 0.34 g of hydrogen peroxide.

After treatment, the pulp has a kappa index equal to 8, with the consumption of hydrogen peroxide to reach this result being only 4.3% by weight with respect to the pulp used.

An analogous result is obtained if one operates at the same temperature as above, but in continuous manner with introduction of the pulp to be bleached and equivalent

output of bleached pulp while recycling the bleaching solution, separated from the extracted pulp and restored to hydrogen peroxide titer and titer of other constitutive ingredients of the bleaching bath such as defined above, in such a manner that in the treatment zone a steady state is established and that contact is ensured during a period of 8 hours between the pulp and the bleaching solution.

While the invention has been described in connection with a preferred embodiment, it is not intended to limit the scope of the invention to the particular form set forth, but, on the contrary, it is intended to cover such alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.

THE CLAIMS [illegible] THE INVENTION ARE AS FOLLOWS:

1. A process for obtaining a high delignified bleached chemical pulp having a kappa index below 10 in a single stage directly from an unbleached chemical pulp while at the same time returning directly recyclable effluents into the bleaching operation comprising contacting said pulp with an aqueous bleaching solution at a temperature from 70°C to 100°C for a time sufficient to bleach said pulp to the degree desired, said aqueous bleaching solution having a pH of from 11 to 11.5 comprising, for each 100 parts by weight, hydrogen peroxide in an amount effective to bleach the pulp, at least one alkaline agent in amount sufficient to maintain the pH between from 11 to 11.5, at least one alkali metal silicate in an amount expressed in SiO_2 at least equal to 0.3% by weight, at least one magnesium salt and at least one calcium salt, in a quantity such that the concentration by weight of each of said alkaline earth metals is between 0.05% and 1%, and at least one sequestering agent capable of maintaining said alkaline earth metal ions in the dissolved state in an overall concentration of sequestering agent of at the most equal to 10% by weight.

2. The process of claim 1 wherein said alkaline metal silicate is sodium silicate.

3. The process of claim 1 or 2 wherein the anions of the magnesium and calcium salts are inert with respect to hydrogen peroxide.

4. The process of claim 1 or 2 wherein the magnesium salt is magnesium chloride and the calcium salt is calcium chloride.

5. A process for obtaining a high delignified bleached chemical pulp having a kappa index below 10 in a single stage directly from an unbleached chemical pulp while at the

same time returning directly recyclable effluents into the bleaching operation comprising contacting said pulp with an aqueous bleaching solution at a temperature from 85°C to 95°C for a time sufficient to bleach said pulp to the degree desired, said aqueous bleaching solution having a pH of from 11 to 11.5 consisting essentially of, for each 100 parts by weight, water, hydrogen peroxide in an amount up to 1% by weight, an alkaline agent selected from sodium hydroxide or sodium carbonate in an amount sufficient to maintain the pH from 11 to 11.5, sodium silicate in an amount expressed in SiO_2 from 0.3% to 20% by weight, calcium chloride in an amount calculated as calcium ion from 0.05% to 1% by weight, magnesium chloride in an amount calculated as magnesium ion from 0.05% to 1% by weight, and at least one sequestering agent for said calcium and magnesium ions in an amount of sequestering agent between that amount effective to maintain said ions in solution and about 10% by weight.

6. An aqueous bleaching solution for use in a process according to claim 1 or claim 5 comprising, for each 100 parts by weight thereof:

	% by Weight
Hydrogen peroxide	up to 1
Alkaline agent	Amount sufficient to maintain pH from 11 to 11.5
Alkali metal silicate (expressed as SiO_2)	0.3 to 20
Calcium salt (as calcium ion)	0.05 to 1
Magnesium salt (as magnesium ion)	0.05 to 1
Sequestering agent for calcium and magnesium	up to 10.

7. The bleaching solution of claim 6 wherein said alkaline agent is selected from sodium hydroxide or sodium carbonate, said alkali metal silicate is sodium silicate,

and said calcium and magnesium salts are chlorides.

8. The bleaching solution of claim 6 or 7 wherein the amount of hydrogen peroxide is from 0.02% to 0.5% and the amount of silicate is from 0.3% to 5%.

DATED this 15th day of September, 1987

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JM:mk (3.10)